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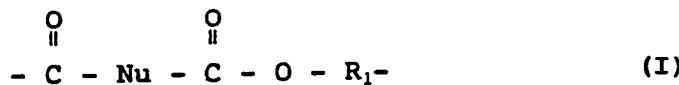
WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08G 18/10, 18/42, 18/76 C09J 3/00		A1	(11) International Publication Number: WO 91/15530 (43) International Publication Date: 17 October 1991 (17.10.91)
(21) International Application Number: PCT/US91/02216	(22) International Filing Date: 29 March 1991 (29.03.91)	(74) Agents: BYRNE, Linda, M. et al.; Merchant, Gould, Smith, Edell, Welter & Schmidt, 1000 Norwest Center, 55 East Fifth Street, Saint Paul, MN 55101 (US).	
(30) Priority data: 502,980 30 March 1990 (30.03.90) US	(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).		
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(54) Title: HOT MELT MOISTURE-CURE POLYURETHANE ADHESIVE



(57) Abstract

Hot melt adhesive compositions combining the characteristics of thermoplastic hot melt adhesives and reactive adhesives can be prepared by blending a polyester polyether thermoplastic elastomer having formula (I) wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous polyether subunit comprising a polyoxalkylene group with a polyisocyanate prepolymer. The resulting composition is flexible and may be used as an adhesive or as a sealant.

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HOT MELT MOISTURE-  
CURE POLYURETHANE ADHESIVE

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Field of the Invention

The invention relates to extrudable moisture-cure hot melt urethane adhesives comprising a urethane prepolymer and a segmented thermoplastic elastomer as well as methods 10 of their manufacture.

Related Art

Hot melt adhesives and moisture-cure urethane adhesives are well known generic adhesive classes. Hot melt adhesives generally comprise thermoplastic materials 15 which can be conveniently applied by extruding the adhesive composition at elevated temperatures onto a workpiece to which it is desired to fix another workpiece. The adhesive bond increases in integrity as the composition cools. Hot melt adhesives generally have good 20 green strength, i.e., initial strength before complete setting of the bond, and they have the additional benefits of being easy to handle and free of solvents which must be evacuated during the setting or curing process of the adhesive. However, hot melt adhesives have the drawback 25 that after cooling to form a bond line, the thermoplastic compositions can be temperature sensitive, in other words, the bonding mass can lose bond strength as the temperature of the work piece and the bond line increase. Further, hot melt adhesives tend to be physically unstable in the

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presence of hydrocarbon solvents and some organic compositions.

In sharp contrast, many curable urethane adhesives have little green strength. Thus, after the application 5 of a curable urethane adhesive, the structure to be bonded must be externally supported until the urethane can cure to a strong, resilient, highly cross-linked bond line. Additionally, solvents may be used in these adhesives which may need to be evaporated during cure. However, 10 once cured, these urethane adhesives have high tensile strength and have little or no temperature sensitivity. They also offer good resistance to many solvents after cure.

Clearly, a single adhesive composition displaying both 15 curing and hot melt properties is a desirable goal, since the resulting adhesive, in theory, could possess quick, high strength green bonding and strong, cross-linked cured adhesive bonding.

One suggested adhesive is Uchigaki et al, U.S. Patent 20 No. 3,931,077 which discloses reactive, high viscosity hot melt adhesive compositions comprising a specific high viscosity reactive urethane prepolymer, a specific ethylene-vinyl acetate thermoplastic polymer and a phenolic or abietic acid type tackifying resin. Uchigaki 25 suggests using ethylene-vinyl acetate thermoplastic copolymers containing 70-90 wt-% ethylene to achieve adhesives having good final adhesive strength.

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Another type of hot melt adhesive is disclosed in U.S. Patent No. 4,585,919 to Reichle et al which teaches the combination of an isocyanate prepolymer, a thermoplastic polyurethane or polyester, and a synthetic resin selected 5 from the group consisting of ketone resins, hydrogenation products of acetophenone condensation resins, and mixtures thereof.

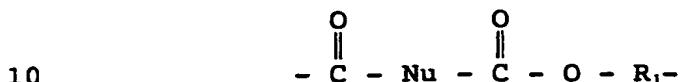
Marhevka et al, U.S. Patent No. 4,775,719 discloses a thermally stable, hot melt moisture-cure polyurethane 10 adhesive composition having a lower viscosity than Uchigaki, comprising an ethylene-vinyl monomer having an ethylene content of 55 wt-% or less, a polyisocyanate prepolymer and an aromatic tackifying resin. Marhevka et al, U.S. Patent No. 4,808,255 discloses a thermally 15 stable, moisture-cure urethane hot melt adhesive comprising a thermoplastic polymer, a compatible, curing urethane polyalkylene polyol prepolymer and a tackifying agent, and U.S. Patent No. 4,820,368 to Marhevka et al discloses a thermally stable, moisture-cure urethane hot 20 melt adhesive comprising a thermoplastic polymer, a compatible, curing urethane polyester polyol prepolymer and a tackifying agent. These adhesives form rigid bonds upon curing.

Summary of the Invention

25 The present invention concerns an improved urethane hot melt adhesive composition having thermal stability that can be extruded to form an initially high green

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strength hot melt bond and which can moisture-cure to an adhesive bond. This adhesive composition comprises about 20 to 95 wt-% of a polyisocyanate prepolymer comprising the reaction product of a polyol and a polyfunctional 5 isocyanate having an isocyanate functionality of about 2 or more and about 5 to 80 wt-% of a polyester polyether copolymer comprising a polymer having the formula



wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous, long-chain polyether subunit comprising a polyoxyalkylene group. This invention also concerns 15 methods of making and using this novel, urethane hot melt adhesive composition. The term "adhesive" as used in the specification and the claims is meant to include both adhesive and sealant compositions.

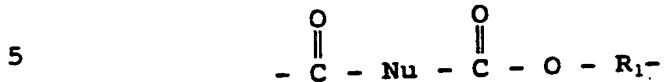
By incorporating the polyester polyether copolymer 20 above, the resulting moisture-cure hot melt achieves a high moisture vapor transmission rate (MVTR) allowing thicker adhesive films, exhibits excellent green strength, adheres well to polar substrates, results in a flexible, cured bond, and which can have residual tack, prior to 25 cure, to act as a pressure-sensitive adhesive.

Detailed Description of the Preferred Embodiment

The present invention is addressed to a novel

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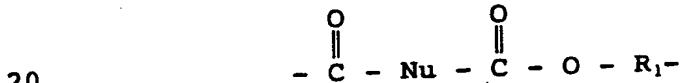
moisture-cure urethane hot melt adhesiv composition which comprises a polyester polyether copolymer having the formula:



wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous, long-chain polyether subunit comprising a 10 polyoxyalkylene group and a polyisocyanate prepolymer comprising the reaction product of a polyol and a polyfunctional isocyanate having an isocyanate functionality of about 2 or more.

Thermoplastic

15 The thermoplastic of the present invention is a segmented thermoplastic with both hard and soft segments. This thermoplastic comprises a polymer having the formula



wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous, long-chain polyether subunit comprising a polyoxyalkylene group. The nucleus is preferably derived 25 from a dicarboxylic acid which may be aromatic or aliphatic. The terms "dicarboxylic acid" and "diacid" as used in the specification and the claims is meant to include dicarboxylic acids, diacids, and their equivalents. The aromatic nucleus may be derived from

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aromatic dicarboxylic acids. Representative aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, phthalic acid, substituted dicarboxy compounds with benzene nuclei such as bis(p-carboxy-phenyl) methane, p-  
5 oxy(p-carboxyphenyl) benzoic acid, ethylene-bis(p-oxybenzoic acid), ethylene-bis-(p-benzoic acid), tetramethylene-bis(p-oxybenzoic acid), 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, phenanthrene dicarboxylic  
10 acid, anthracene dicarboxylic acid, 4,4'-sulfonyl dibenzoic acid, indene dicarboxylic acid, and the like as well as ring substituted derivatives thereof such as C<sub>2-10</sub> alkyl, halo, alkoxy or aryl derivatives. Hydroxy acids such as p(β-hydroxyethoxy) benzoic acid can also be used  
15 providing an aromatic dicarboxylic acid is also present.

Preferably the precursor to the nucleus is a methyl ester of the dicarboxylic acid. More preferably, the nucleus is derived from dimethyl isophthalate, dimethyl terephthalate, dimethyl cyclohexane dicarboxylate or  
20 mixtures thereof. Most preferably, the nucleus is a aromatic nucleus derived from a mixture of dimethyl isophthalate and dimethyl terephthalate.

The characteristics of R<sub>1</sub> determine whether the segment is a hard or a soft segment. In a hard segment, R<sub>1</sub> is a C<sub>2-6</sub> alkylene group, and it is preferably derived from aliphatic, alicyclic, or aromatic short chain diols with molecular weights of less than about 250. Preferably

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these diols are those with 2-15 carbon atoms such as ethylene, propylene, tetramethylene, isobutylene, pentamethylene, 2,2-dimethyltrimethyl n, hexamethylene, and decamethylene glycols, dihydroxycyclohexane, 5 cyclohexane dimethanol, resorcinol, hydroquinone, 1,5-dihydroxynaphthalene, and the like. Especially preferred are the aliphatic diols of 2 to 6 carbon atoms. Suitable bisphenols include bis(p-hydroxydiphenyl), bis(p-hydroxyphenyl) methane, bis(p-hydroxyphenyl) methane, 10 bis(p-hydroxyphenyl) propane and 2,2-bis(p-hydroxyphenyl) propane. Equivalent ester forming derivatives of diols are also useful. These diol derivatives may be used to form the diol in situ prior to forming the hard segment.

15 The soft segments are formed when  $R_1$  is an amorphous, long chain polyether subunit. This subunit should have a molecular weight of about 350 to about 6,000, preferably about 350 to about 3,000 and most preferably from about 1,000 to about 3,000, a melting point of less than about 20 55° C. and a carbon:oxygen ratio of greater than about 2.5:1. Representative polyethers include the poly(alkylene oxide) glycols wherein alkylene is  $C_{2-6}$  such as poly(1,2-and 1,3-propylene oxide) glycol, poly(tetramethylene oxide) glycol, poly(pentamethylene oxide) glycol, poly(hexamethylene oxide) glycol and poly(1,2-butylene oxide) glycol; random or block copolymers of ethylene oxide and 1,2-propylene oxide (used in

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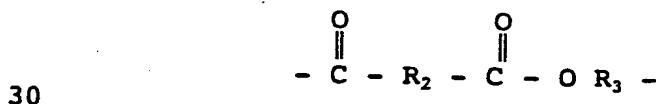
proportions such that the carbon to oxygen m le ratio in the glycol exceeds 2.5:1) and poly-formals prepared by reacting formaldehyde with glycols, such as pentamethylene glycol, or mixtures of glycols, such as a mixture of 5 tetramethylene and pentamethylene glycols.

Again, derivatives of the polyol may be used to form polyether subunit in situ prior to formation of the thermoplastic.

Preferably the polyether subunit comprises a 10 polyoxyalkylene polyol having from 2 to 6 carbon atoms in the alkylene group. Most preferably, the polyoxyalkylene polyol comprises polytetramethylene ether glycol (PTMEG). "Polyol" as used herein the specification and the claims includes both diols and triols. One class of polyester 15 polyether thermoplastic comprises compositions which comprise, based on the total thermoplastic components, (A) about 1 to 99 percent by weight of thermoplastic segmented copolyester elastomer consisting essentially of a multiplicity of recurring short chain ester units and long 20 chain ester units joined through ester linkages, said short chain ester units amounting to about 15 to 75 percent by

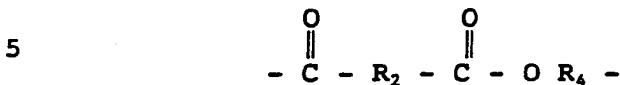
weight of said copolyester and being of the formula

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and said long chain ester units amounting to about 25 to 85 percent by weight of said copolyester and being of the formula



wherein  $\text{R}_2$  is the divalent aromatic radical remaining after removal of the carboxyl groups from aromatic dicarboxylic acid having a molecular weight of less than about 350,  $\text{R}_3$  is the divalent radical remaining after removal of the hydroxyl groups from organic diol having a molecular weight of less than about 250, and  $\text{R}_4$  is the divalent radical remaining after removal of the terminal hydroxyl groups from long chain glycol or polyalkylene glycol having an average molecular weight of about 350 to 6000, said copolyester having a melt index of less than about 150 and a melting point of at least about 125°C., and (B) about 1 to 99 percent by weight of low molecular weight thermoplastic resin which forms compatible mixtures with the segmented copolyester, is thermally stable at 150°C., and has a melt viscosity of less than about 10,000 centipoises at 200°C. These compositions are disclosed in U.S. Pat. Nos. 3,832,314; 3,932,326; and 3,959,062 to Hoh et al, which references are herein incorporated by reference. Especially preferred are compositions according to the above formulas wherein  $\text{R}_2$  is derived from terephthalic acid or a mixture of terephthalic and isophthalic acids,  $\text{R}_3$  is derived from an organic diol such

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as butanediol and R<sub>4</sub> is derived from a long chain glycol such as polytetramethylene ether glycol (PTMEG).

Additionally, other thermoplastic components which will not detrimentally affect the adhesive character of 5 the composition may be incorporated into the adhesive composition. Representative examples of these thermoplastic components include compatible vinyl polymers such as vinyl acetate-ethylene copolymers, ethylene-vinyl acetate and vinyl alcohol copolymers; and ethylene acrylic 10 compounds including ethylene acrylate copolymers, ethylene methacrylate, ethylene butylacrylate, and ethylene hydroxyethyl acrylate. Preferably, the thermoplastic components comprise a vinyl polymer, a vinyl acetate-ethylene copolymer, or mixtures thereof. More preferably, 15 the optional thermoplastic component comprises a high vinyl acetate content vinyl acetate-ethylene copolymer. Most preferably, this vinyl acetate-ethylene copolymer comprises about 40% to about 60% vinyl acetate.

20

#### Prepolymer

The polyisocyanate prepolymer of the present invention 25 comprises the reaction product of a polyol and a polyfunctional isocyanate having an isocyanate functionality of about 2 or more. The polyol of the

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present invention may be either a poly ether polyol, a polyester polyol, or mixtures thereof. Preferably, the polyol is a polyether polyol or a mixture of a poly ether polyol and a polyester polyol. The polyether polyol is 5 preferably a polyoxyalkylene polyol wherein the alkylene is C<sub>2-8</sub>. Representative polyoxyalkylene polyols included the poly(alkyleneoxide) glycols wherein alkylene is C<sub>2-8</sub> such as poly(1,2- and 1,3-propylene oxide) glycol, poly(tetramethylene oxide) glycol, poly(pentamethylene 10 oxide) glycol, poly(hexamethylene oxide) glycol, poly(heptamethylene oxide) glycol, poly(octamethylene oxide) glycol, poly(nonamethylene oxide) glycol and poly (1,2-butylene oxide) glycol; random or block copolymers of ethylene oxide and 1,2-propylene oxide (used in 15 proportions such that the carbon to oxygen mole ratio in the glycol exceeds 2.5) and poly-formals prepared by reacting formaldehyde with glycols, such as pentamethylene glycol, or mixtures of glycols, such as a mixture of tetramethylene and pentamethylene glycols. Additionally, 20 the dicarboxymethyl acids of polyoxyalkylene polyols can be used to form long chain polyols in situ as is known by those skilled in the art.

However, the preferred polyoxyalkylene polyol for use in the prepolymer of the present invention is 25 polytetramethylene ether glycol (PTMEG). Most preferably, the polyol of the prepolymer is the same as that polyol used in the polyether polyester thermoplastic elastomer of

the adhesiv .

When mixtures of polyols are used in th pr polym r, the polyols must have partial compatibility with the polyether polyester thermoplastic used in the adhesive.

5 The polyester polyols contemplated for use in the prepolymer of the present invention include those which are the reaction products of various polyols with aromatic or aliphatic dicarboxylic acids and polymers of lactones (e.g., polycaprolactone). Representative examples of the 10 aromatic acids which may be used include teraphthalic acid, isophthalic acid and phthalic anhydride, Representative examples of aliphatic acids include sebasic acid, adipic acid and glutaric acid. Representative examples of polyols include ethylene glycol, butane diol, 15 neopentylglycol, hexane diol, propylene glycol, dipropylene glycol, diethylene glycol and cyclohexane dimethanol.

The isocyanate used in the present invention is generally a cyclic polyfunctional isocyanate with a 20 functionality of about 2 or more. Preferably, the functionality is about 2. The isocyanate may be aromatic or aliphatic. Representative examples of aromatic isocyanates include diphenyl methylene diisocyanate, tetramethyl xylene diisocyanate, isophorone diisocyanate, 25 toluene diisocyanate. Representative examples of aliphatic diisocyanates include hexamethylene diisocyanate, hydrogenated MDI, napthalene diisocyanate,

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dodecane isocyanate, dimer diisocyanate and all polymeric, trimeric isocyanates. Preferably, the isocyanate comprises diphenyl methylene diisocyanate, tetramethylxylene diisocyanate, isopherone diisocyanate, 5 toluene diisocyanate, hexamethylene diisocyanate or mixtures thereof. Most preferably, the isocyanate comprises diphenyl methylene diisocyanate.

The isocyanate prepolymer may be stripped to less than 0.5% free isocyanate monomer. One device useful for 10 stripping unreacted isocyanate monomer is a wipe film evaporator. The use of stripped isocyanate prepolymer can result in improved safety in handling the adhesives.

Optional Components

To improve the tack, and to impart pressure sensitive 15 qualities to the adhesive, a tackifier may be incorporated into the adhesive composition. This tackifier may be a rosin ester, an aromatic resin, or mixtures thereof. Representative examples of rosin esters which are useful in the present invention include glycerol rosin ester, 20 pentaerythritol rosin ester, and hydrogenated version of the above. Representative examples of aromatic resins include alphamethyl styrene resin, styrene monomer, polystyrene, coumorone, indene, and vinyl toluene. Preferably, the tackifier is an aromatic resin, and more 25 preferably it is a styrene resin. Most preferably, the tackifier is alphamethyl styrene resin.

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Fillers may be incorporated into the adhesive composition in the form of particulate matter, fibers, or powders. These fillers may be any filler materials which will not interfere with the other components in the adhesive composition. Types of fillers include calcium carbonate, 5 ceramics, glass, silica, quartz, mica, treated clay, titanium dioxide, boron nitrides, graphite, carbon black, asbestos, metals, barium, sulfate, talc, or mixtures thereof. Preferred fillers include calcium carbonate, silica, clay, carbon black, or mixtures thereof.

10 Plasticizers may also be incorporated into the adhesive composition of the present invention. The plasticizer may be any composition which does not interfere with the efficacy of the other components and which facilitates processing and increases toughness and flexibility of the adhesive 15 composition. Representative plasticizers include liquid aromatic ester plasticizers including dioctyl phthalate esters; solid plasticizers including dicyclohexyl phthalate, cyclohexane dimethanol dibenzoate; and the plasticizers available under the SANTICIZER trademark available from 20 Monsanto.

In addition to the above indicated optional components, various other compounds may be added to the adhesive composition. These compounds include catalysts, dyes, inhibitors, antioxidants, UV absorbers, waxes, adhesion

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promotors (e.g., silane) and other conventional additives.

#### Selection of Components

The selection of components for use in the adhesive 5 composition depend upon its use in a variety of applications. Several possibilities follow, and they are not intended to be limiting of the possible combinations of components in the adhesive composition. First, the polyol of the prepolymer and that of the polyether polyester thermoplastic portion 10 must be at least partially compatible. This results in a homogeneous adhesive composition with superior qualities. Preferably the polyols used in the two components are equivalent polyols, and most preferably they are the same polyol.

15 Improvements in residual tack of the adhesive composition may be obtained by incorporating selected tackifiers in the composition. Indeed, adhesives of the present invention can exhibit excellent pressure sensitive attributes when various tackifiers are used. However, tackifiers selected must be 20 at least partially compatible with the polyether polyester thermoplastic and prepolymer components.

#### Preparation

#### Proportions of Reactants

The thermoplastic portion of the composition is separated 25 into two parts: the polyester polyether thermoplastic and

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the compatible vinyl polymer. The thermoplastic is present from about 5 to about 80 wt-% of the adhesive composition. Preferably, it is present at about 5 to about 50 wt-%, and most preferably it is present at about 5 to about 35 wt-%.

5 The optional compatible vinyl polymer is present at about 0 to about 30 wt-%. Preferably it is used at about 5 to 25 wt-% and most preferably at about 5 to about 20 wt-%.

10 The isocyanate prepolymer is present at about 20 to about 95 wt-% of the adhesive composition. Preferably it is present at about 20 to about 50 wt-% and most preferably at about 25 to about 45 wt-%.

15 The tackifier is present at about 0 to about 60 wt-%, preferably from about 15 to about 50 wt-% and most preferably at about 25 to about 45 wt-%.

15 Silane may be incorporated in the composition for certain applications. It is present at about 0 to about 2 wt-%, and preferably it is present at about 0.5 to about 1 wt-%. Additionally, a filler may be present at about 0 to about 50 wt-%, plasticizer at about 0 to about 10 wt-% and a catalyst 20 at about 0 to about 1.0 wt-%.

25 There are numerous methods of preparation of the adhesive composition of the present invention. Many of these will be obvious to those skilled in the art. One such variation is that the prepolymer may be prepared separately or simultaneously with the preparation of the adhesive

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composition.

Method of Use

For use as an adhesive or sealant, the solid composition can be placed into a drum or pail, and platen type dispensing equipment can be used to deliver the adhesive. The adhesive can be extruded at about 95 to about 175° C. onto a substrate. Prior to the moisture-cure of the adhesive, a second substrate is contacted with the adhesive. The adhesive exhibits sufficient green strength such that external mechanical support is not needed while the adhesive moisture-cures. Substrates suitable for use with the adhesive of the present invention include glass, metal, polycarbonate, acrylic, ABS, PVC, vinyl, wood, etc.

The reactive hot melt urethane adhesive compositions of the invention can be cured in the bond line using a variety of mechanisms. The curing reaction occurs between a compound having an available active hydrogen atom and the NCO groups of the polyurethane prepolymer. A variety of reactive compounds having free active hydrogens are known in the art including water, hydrogen sulfide, polyols, ammonia, and other active compounds. Such curing reactions can be conducted by relying on the presence in the atmosphere such as moisture, of the active compounds or the active compounds can be added to the adhesive at the bond line.

One of the novel features of the adhesive of the present

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invention over the current state of the art is its higher moisture vapor transmission rate (MVTR) and CO<sub>2</sub> transmission rate. The adhesive can be applied in thicker beads, films or bond lines resulting in a thicker adhesive mass without 5 foam formation.

Examples

The following specific examples, which contain the best mode, can be used to further illustrate the invention.

Example I

10 A polyisocyanate prepolymer was prepared by the following process. A reactor was charged with about 78 parts of a molten polytetramethylene ether glycol having a molecular weight of about 2900, and it was mixed under vacuum for about 30 minutes at about 75-80°C. The vacuum was broken by 15 establishing a nitrogen atmosphere over the molten polyol. About 22 parts of diphenylmethylenediiisocyanate flakes were added to the reactor under positive nitrogen pressure at about 75°C. The resulting reaction was allowed to proceed until the prepolymer product was less than about 5% NCO. The 20 prepolymer was then discharged into and stored in clean, dry cans under a nitrogen blanket.

Example II

15 parts of a polyester polyether thermoplastic having a differential scanning colorimeter melting point of 123°C 25 and a melt index (ASTM D 1238) at 190°C of 6 was added to a

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small jar and heated to 177° C. for 2 hours. About 15 parts of the polyisocyanate prepolymer of Example I was added to the melt and blended into it at 177 C. The melt composition had a viscosity of greater than 100,000 cps and on cooling, 5 it had outstanding green strength and elastomeric properties. After 3 days the adhesive had increased substantially in tear and tensile strength.

A portion of the material is poured onto a nonstick surface and drawn into a film that was approximately 120 10 thousands of an inch thick. The material was allowed to cool overnight and then to cure at 25°C and 50% relative humidity for 5 days. An ASTM type 5 die was used to cut the film into dogbones. The resulting tensile strength (an average of six samples) run at 10 inches per minute was 2400 psi with an 15 elongation at maximum load of 850%. The cured film was very elastic and has high rebound.

### Example III

A formulation incorporating a tackifier and a vinyl 20 acetate-ethylene copolymer was prepared according to the following procedures. A premix of 80 g of an aromatic alphamethyl styrene tackifying resin having a ring and ball softening point of 97 to 103°C and 80 g of a polyester polyether thermoplastic having a vicat softening point (ASTM 25 D1525) of 80°C and a melting point (ASTM D3418) of 159°C was

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mixed at 375° F. until molten. An additional 240 g of the aromatic alphamethyl styrene tackifying resin and 80 g of an ethylen -vinyl acetate copolymer having a melt index of 3.5 and 51 wt-% vinyl acetate were added to the mixer, and a 5 vacuum was established over the resulting melt for about 30 minutes. 320 g of the polyisocyanate prepolymer of Example I (except that the unreacted MDI is reduced to < 0.5% in a wipe film evaporator) were added and mixed into the melt, and again a vacuum was established over the mixture for about 30 10 minutes. The mixture was then poured into containers and allowed to cool. Properties of the adhesive are shown below in Table I.

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Table I

Test Results of an Adhesive  
According to the Present Invention

5	PHYSICAL PROPERTY	TEMPERATURE (°F)	AVERAGE VALUE
	7 DAY TENSILE	RT	2000 psi
	7 DAY ELONGATION	RT	2600 %
	14 DAY TENSILE	RT	3600 psi
10	14 DAY ELONGATION	RT	2400 %
	21 DAY TENSILE	RT	3500 psi
	21 DAY ELONGATION	RT	2300 %
	28 DAY TENSILE	RT	4400 psi
	28 DAY ELONGATION	RT	2400 %
15	14 DAY 200 g PAFTS	N/A	313 °F
	14 DAY 500 g SAFTS	N/A	350 °F
	VISCOSITY	300	100000 cP
	VISCOSITY	310	58000 cP
	VISCOSITY	320	31500 cP
20	VISCOSITY	330	14000 cP
	VISCOSITY	340	10000 cP
	VISCOSITY	350	8250 cP
	VISCOSITY	360	7000 cP

25 Comparative Example A

About 47.5 parts of an aromatic alphamethyl styrene tackifying resin having a ring and ball softening point of 97 to 103°C and about 10 parts of ethylene-vinylacetate copolymer having a melt index of 3.5 and 51 wt-% vinyl acetate were added to a mixer at about 190°C and mixed for about 30 minutes under vacuum. About 42.5 parts of the polyisocyanate prepolymer of Example I were added to the mixer and the composition was mixed under vacuum for about 30 minutes. The composition was then poured into containers and allowed to cool. Properties of the adhesive and a film drawn down from the above composition are illustrated in

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Table II.

Table II  
Test Results of an Adhesive  
According to the Current State of the Art

5	PHYSICAL PROPERTY	TEMPERATURE (°F)	AVERAGE
10	7 DAY TENSILE	RT	2200 psi
	7 DAY ELONGATION	RT	2300 %
14	14 DAY TENSILE	RT	3100 psi
	14 DAY ELONGATION	RT	2100 %
21	21 DAY TENSILE	RT	3500 psi
	21 DAY ELONGATION	RT	1800 %
28	28 DAY TENSILE	RT	3900 psi
	28 DAY ELONGATION	RT	1500 %
15	14 DAY 200 g PAFTS	N/A	321 °F
	14 DAY 500 g SAFTS	N/A	325 °F
20	VISCOSITY	300	4100 cP
	VISCOSITY	310	3413 cP
25	VISCOSITY	320	2775 cP
	VISCOSITY	330	2313 cP
	VISCOSITY	340	2000 cP
	VISCOSITY	350	1775 cP
	VISCOSITY	360	1600 cP

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The initial handling strength was estimated by testing maple block shear strength (at 0.015 inches/minute) as a function of time (25°C / 50% relative humidity) after bond formation. The adhesive of Example III was compared to the adhesive of Comparative Example A. The results, illustrated in Table III, show that the adhesive of Example III has improved handling strength and cure rate.

Table III  
Maple Block Shear Strength

	<u>Time</u>	<u>Example III</u>	<u>Comparitive Example A</u>
	15 minutes	6 psi	3 psi
	1 hour	6 psi	1 psi
	4 hours	9 psi	1 psi
	1 day	41 psi	2 psi
10	4 days	550 psi	2 psi
	7 days	480 psi	550 psi

Example IV

255.9 g hexane diol was heated in an oven at 60°C prior  
 15 to use. 288.0 g Isophthalic Acid, 255.9 g hexane diol and  
 2.75 g of an antioxidant were added to a reactor flask. The  
 reactor was then heated beyond 100° C. at which time 3.3 g  
 hydrated monobutyl tin oxide catalyst were added. The  
 temperature was increased to 240° C. and held for two hours  
 20 during which time the mixture became clear. A vacuum was  
 established over the mixture for about one hour until the  
 acid number fell to less than 2. The mixture was then poured  
 onto a flat surface and allowed to cool and crystallize to  
 form an IPA-HD polyol. 68.1 g of the IPA-HD polyol prepared  
 25 above, 175.8 g of a polytetramethylene ether glycol having  
 a molecular weight of about 2900 which was premelted at about  
 95°C, and 145.5 g of a polyester polyether thermoplastic  
 having a vicat softening point (ASTM D1525) of 80°C and a

- 24 -

melting point (ASTM D3418) of 159°C were added to a flask and heated to 180° C. A vacuum was established over the mixture, and the heat was reduced. Once the mixture reached about 170° C. mixing was stopped and flakes of pure 5 diphenylmethylene diisocyanate were added. The mixing was recommenced, and the mixture was heated up to 180° C. After the mixture was homogeneous, it was cooled and poured into quart cans under nitrogen atmosphere. The material was somewhat cloudy in appearance and easy to pour.

10

Example V

280 g of an aromatic alphamethyl styrene tackifying resin having a ring and ball softening point of 97 to 103°C, 80 g of an ethylene-vinyl acetate copolymer having a melt index of 18 and 51 wt-% vinyl acetate, and 120 g of a polyester 15 polyether thermoplastic having a vicat softening point (ASTM D1525) of 80°C and a melting point (ASTM D3418) of 159°C were mixed at about 195°C and evacuated for about 30 minutes. 320 g of a prepolymer made as in Example I (except that the unreacted MDI was reduced to <0.5% in a wipe film evaporator) 20 was added, mixed for about 30 minutes and the material was evacuated for an additional 30 minutes and then poured into metal containers. SAFT after a two week cure at 50% R. H. at room temperature was > 175°C. PAFT after a two week cure at 50% R. H. at room temperature was about 160°C. Tensile 25 strength was 3300 psi and elongation was 230% after a two

- 25 -

week cure at 50% R. H. at room temperature.

Example VI

5        35 parts of an aromatic alphamethyl styrene tackifying resin having a ring and ball softening point of 97 to 103°C and 25 parts of polyester polyether thermoplastic having a vicat softening point (ASTM D1525) of 80°C and a melting point (ASTM D3418) of 159°C were mixed at about 195°C. 40  
10      parts of a prepolymer made as in Example I (except that the unreacted MDI was reduced to < 0.5% in a wipe film evaporater) was added and mixed and then poured into metal containers. SAFT after a two week cure at 50% R. H. at room temperature was > 145°C. PAFT after two week a cure at 50%  
15      R. H. at room temprature was about 160°C.

The Examples and data shown above indicate that the compositions of the invention can be blended into reactive hot melt urethane adhesives having both hot melt and curing adhesive properties. The adhesives can be blended to have 20 cured bonds with superior heat resistance. Further, the cured adhesives can have ultimate tensile strengths in the range of about 2,000 to 4,400 psi and ultimate elongation at break in the range of about 850 to 2,600%. Such data indicates that the blended components cooperate to provide 25 the combined properties of a hot melt adhesive and achieved

- 26 -

curing urethane adhesive properties. Further, the adhesives can be blended to have superior heat resistance.

The data shown above were developed using the following procedures.

5

200 Gram Peal Test (PAFT)

500 Gram Shear Test (SAFT)

Scope:

Kraft paper is laminated to form a one inch by one inch bond area. Weights are attached in the peel and shear modes and the samples are placed in an oven. The oven is programmed to increase temperature at a certain rate. The temperature at which the bond delaminates is recorded.

Equipment:

- 15 1. Programmable oven capable of a 25% C. per hour increase from 25° C. to 150° C.
2. 40 pound basis weight kraft paper.
3. 200 and 500 gram weights.
4. Device for monitoring oven temperatures.
- 20 5. Device for supporting samples in the oven.
6. Release paper.
7. Two glass rods, each one-half inch in diameter and eight inches long. One glass rod should have a ten mil shim at each end.

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Sample Preparation

1. Cut two sheets of kraft paper, each six inches by twelve inches.
2. Cut two pieces of release paper, each two inches by 5 twelve inches.
3. Tape one piece of kraft paper to a heat insulator such as a tablet back, heavy chip board, etc.
4. Tape the two pieces of release paper to the kraft lengthwise in the center, exactly one inch apart.
- 10 5. Lay the second piece of kraft paper on top of the release paper so it entirely covers the first piece of kraft paper. Tape one end only of the second piece of kraft to the composite.
- 15 6. Fold back the second piece of kraft and place the shimmmed glass rod on the tape "hinge".
7. Place the unshimmmed glass rod below the second sheet of kraft paper as close to the tape "hinge" as possible. (The second piece of kraft is now between the two glass rods. The shimmmed rod is on top in view. The unshimmmed rod is 20 partially concealed by the second piece of kraft because it is folded back.)
8. Pour a stream of hot melt at its normal application temperature, (e.g., 350° F.) onto the first piece of kraft between the release paper.
- 25 9. Quickly push both glass rods across the bottom sheet

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of kraft paper. (The shimmed glass rod will draw the hot melt into a film, and the second rod will pull the second piece of kraft paper over the first to form a bond.)

10. Trim the "sandwich" widthwise to four inches and 5 lengthwise to six inches.

11. Cut the "sandwich" widthwise into six pieces, each one inch by four inches.

12. Allow bonds to fully cure in a room at 50% RH, 25° C.

10 Procedure:

1. Suspend the six samples, from one "tail" in the oven.

2. Attach a 200 gram weight to a tail of each of three samples in the peel mode.

3. Attach a 500 gram weight to a tail of each of three 15 samples in the shear mode.

4. Start the oven at 25° C. and increase the temperature continuously at 25° C./hour.

5. Observe the samples and note the temperature at which the samples delaminate and the weight falls.

20 Report:

Report the average temperature at which the three peel and three shear samples fail.

Tensile/Elongation Test

Scope:

25 This test procedure describes the method whereby the

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tensile characteristics can be determined at a constant strain rate.

Equipment:

1. Instron tensile tester or equivalent.
- 5 2. Teflon drawdown sheet.
3. ASTM D-412 Type C die..
4. Micrometer.

Sample Preparation:

1. Prepare a 20-30 mil adhesive film. The film must be 10 void free.
2. Allow the film to cure at a room at 50% RH, 25° C.
3. Cut at least five samples from the film with the ASTM D-412 Type 5 die.
4. Measure the film thickness of each sample at the 15 gauge section in the middle and record. If properly cut, the sample should have a gauge section width of 0.25 inches, but check to be sure.
5. Condition the samples for at least 18 hours at 25° C., 50% relative humidity.

20 Test Procedure:

1. Set the tensile tester jaws to a 2" gap, and attach the sample.
2. Elongate at the constant strain rate of 10" per minute until the sample breaks, while recording the stress 25 versus strain.

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3. Rep at steps 1 and 2 with the r maining samples.

Calculations:

1. Tensile stress - calculate the tensile by dividing  
5 the force by the cross-sectional area of the sample.

2. Strain elongation - calculate the elongation by  
dividing the sample length or tensile tester jaw gap at the  
point in question by the initial sample gap and multiply by  
100%.

10 Report:

1. Elongation at break as the average of at least 5  
samples.

2. Ultimate tensile and elongation at the highest point  
of stress as the average of at least 5 samples.

15 3. Tensile and elongation at the yield point as the  
average of at least 5 samples.

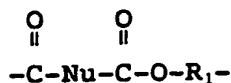
The specification, Examples, data and discussion set  
forth above provide a detailed disclosure of the invention.  
However, since a variety of embodiments of the invention can  
20 be made without departing from the spirit and scope of the  
invention, the invention resides in the claims hereinafter  
appended.

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WHAT IS CLAIMED IS:

1. A urethane hot melt adhesive composition having thermal stability that can be extruded to form an initially high green strength hot melt bond and can moisture-cure to 5 an adhesive bond, which composition comprises:

(a) about 5-80 wt-% of a polyester polyether copolymer comprising a polymer having the formula:



10

wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous, long-chain polyether subunit comprising a polyoxyalkylene group; and

15

(b) about 20-95 wt-% of a polyisocyanate prepolymer comprising the reaction product of:

(i) a polyol; and

(ii) a polyfunctional isocyanate having an isocyanate functionality of about two or more.

20

2. The composition of claim 1 in which Nu is derived from a cyclic diacid.

3. The composition of claim 2 in which the cyclic diacid comprises an aromatic diacid.

4. The composition of claim 3 in which the aromatic diacid comprises terephthalic acid or isophthalic acid or 25 mixtures thereof.

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5. The composition of claim 1 in which the long-chain subunit comprises a polyether glycol moi ty.

6. The composition of claim 5 in which the poly ther glycol moiety comprises a polytetramethylene ether glycol 5 moiety.

7. The composition of claim 1 in which the polyol comprises a polyether polyol, a polyester polyol, a polyalkylene polyol or mixtures thereof.

8. The composition of claim 7 in which the polyol 10 comprises a polyether polyol.

9. The composition of claim 8 in which the polyether glycol comprises polytetramethylene ether glycol.

10. The composition of claim 1 in which the isocyanate comprises diphenylmethlene diisocyanate, tetramethyl xylene 15 diisocyanate, isophorone diisocyanate, toluene diisocyanate, hexamethylene diisocyanate or mixtures thereof.

11. The composition of claim 10 in which the isocyanate comprises diphenylmethlene diisocyanate.

12. The composition of claim 1 which further comprises 20 about 0.5-2 wt-% of a silane compound.

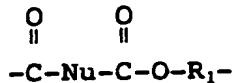
13. The composition of claim 12 in which the silane compound comprises n-methylaminopropyltrimethoxysilane.

14. A urethane hot melt adhesive composition having thermal stability that can be extruded to form an initially 25 high green strength hot melt bond and can moisture cure to

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an adhesive bond, which composition comprises:

(a) about 5-65 wt-% of a polyester poly ether copolymer comprising a polymer having the formula:



wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous, long-chain polyether subunit comprising a polyoxyalkylene group;

10 (b) about 25-85 wt-% of a polyisocyanate prepolymer comprising the reaction product of

(i) a polyol; and

15 (ii) a polyfunctional isocyanate having an isocyanate functionality of about two or more; and

(c) about 10-60 wt-% of a tackifier.

15. The composition of claim 14 in which Nu is derived from a cyclic diacid.

16. The composition of claim 15 in which the cyclic 20 diacid comprises an aromatic diacid.

17. The composition of claim 16 in which the aromatic diacid comprises terephthalic acid, a isophthalic acid or mixtures thereof.

18. The composition of claim 14 in which the long-chain 25 subunit comprises a polyether glycol moiety.

19. The composition of claim 18 in which the polyether

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glycol moiety comprises a polytetramethyl n ether glycol moiety.

20. The composition of claim 14 in which the polyol comprises a polyether polyol, a polyester polyol, a 5 polyalkylene polyol or mixtures thereof.

21. The composition of claim 20 in which the polyol comprises a polyether polyol.

22. The composition of claim 21 in which the polyether glycol comprises polytetramethylene ether glycol.

10 23. The composition of claim 14 in which the isocyanate comprises diphenylmethylenediisocyanate, tetramethyl xylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, hexamethylene diisocyanate or mixtures thereof.

24. The composition of claim 23 in which the isocyanate 15 comprises diphenyl methylene diisocyanate.

25. The composition of claim 14 in which the tackifier comprises a rosin ester, an aromatic resin, or mixtures thereof.

26. The composition of claim 25 in which the tackifier 20 comprises an aromatic resin.

27. The composition of claim 26 in which the aromatic resin comprises alphamethyl styrene, styrene monomer, coumorone, indene vinyl toluene, or mixtures thereof.

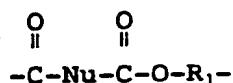
28. The composition of claim 14 which further comprises 25 about 0.5-2 wt-% of a silane compound.

- 35 -

29. The composition of claim 28 in which the silane compound comprises n-methylaminopropyltrimethoxysilane.

30. A urethane hot melt adhesive composition having thermal stability that can be extruded to form an initially high green strength hot melt bond and can moisture cure to an adhesive bond, which composition comprises:

(a) about 5-60 wt-% of a polyester polyether copolymer comprising a polymer having the formula



wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous, long-chain polyether subunit comprising a 15 polyoxyalkylene group;

(b) about 25-80 wt-% of a polyisocyanate prepolymer comprising the reaction product of

(i) a polyol; and

20 (ii) a polyfunctional isocyanate having an isocyanate functionality of about two or more;

(c) about 5-30 wt-% of a compatible vinyl polymer;

and

(d) about 10-60 wt-% of a tackifier.

31. The composition of claim 30 in which Nu is derived 25 from a cyclic diacid.

32. The composition of claim 31 in which the cyclic

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diacid comprises an aromatic diacid.

33. The composition of claim 32 in which the aromatic diacid comprises terephthalic acid, isophthalic acid or mixtures thereof.

5 34. The composition of claim 30 in which the long-chain subunit comprises a polyether glycol moiety.

35. The composition of claim 34 in which the polyether glycol moiety comprises a polytetramethylene ether glycol moiety.

10 36. The composition of claim 30 in which the polyol comprises a polyether polyol, a polyester polyol, a polyalkylene polyol or mixtures thereof.

37. The composition of claim 36 in which the polyol comprises a polyether polyol.

15 38. The composition of claim 37 in which the polyether glycol comprises polytetramethylene ether glycol.

39. The composition of claim 30 in which the isocyanate comprises diphenylmethane diisocyanate, tetramethyl xylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, 20 hexamethylene diisocyanate, toluene diisocyanate, hexamethyl diisocyanate, dicyclohexyl methane diisocyanate or mixtures thereof.

40. The composition of claim 39 in which the isocyanate comprises diphenylmethane diisocyanate.

25 41. The composition of claim 30 in which the tackifier

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comprises a rosin ester, an aromatic resin, or mixtures thereof.

42. The composition of claim 41 in which the tackifier comprises an aromatic resin.

5 43. The composition of claim 42 in which the aromatic resin comprises alphamethyl styrene, styrene monomer, coumorone, indene, vinyl toluene or mixtures thereof.

10 44. The composition of claim 30 in which the compatible vinyl polymer comprises a high vinyl acetate content ethylene vinyl acetate copolymer, an ethylene acrylic or mixtures thereof.

45. The composition of claim 44 in which the ethylene vinyl acetate copolymer comprises about 40-60 wt-% vinyl acetate.

15 46. The composition of claim 30 which further comprises about 0.5-2 wt-% of a silane compound.

47. The composition of claim 46 in which the silane compound comprises n-methylaminopropyltrimethoxysilane.

48. A motor vehicle comprising:

20 (a) a frame;

(b) a window; and

25 (c) a urethane hot melt adhesive composition having thermal stability that can be extruded to form an initially high green strength hot melt bond and can moisture cure to an adhesive bond disposed on at least

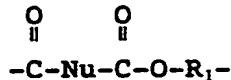
- 38 -

a portion of one surface of the window, which composition comprises:

(i) about 5-80 wt-% of a polyester polyether

5

copolymer comprising a polymer having the formula



10 wherein Nu is a predominately cyclic nucleus and R<sub>1</sub> is randomly selected from either a C<sub>2-6</sub> alkylene or an amorphous, long-chain polyether subunit comprising a polyoxyalkylene group; and

(ii) about 20-95 wt-% of a polyisocyanate prepolymer comprising the reaction product of

(a) a polyol; and

(b) a polyfunctional isocyanate having

an

isocyanate functionality of about two or more;

20 wherein the adhesive disposed on the window is contacted to the frame such that a green bond is formed, the adhesive bond is then exposed to water vapor thereby causing a cross-linking reaction within the adhesive, thereby forming moisture-cured adhesive bond.

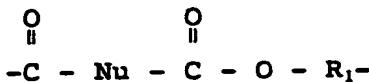
25 49. The motor vehicle of claim 48 in which the polyisocyanate prepolymer further comprises about 0.5 to 2

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wt-% of a silane compound.

50. A urethane hot melt adhesive composition having thermal stability that can be extruded to form an initially high green strength hot melt bond and can moisture cure to 5 an adhesive bond, which composition comprises:

(a) about 5 - 15 wt-% of a polyester polyether copolymer comprising a polymer having the formula



wherein Nu is derived from a mixture of isophthalic acid and terephthalic acid and R<sub>1</sub> is randomly selected from either a C<sub>4</sub> alkylene or an amorphous, long-chain polyether subunit 15 comprising a polyoxyalkylene group derived from polytetramethylene ether glycol;

(b) about 30-50 wt-% of a polyisocyanate prepolymer comprising the reaction product of

20 (i) polytetramethylene ether glycol and  
(ii) diphenylmethane diisocyanate;

(c) about 5-15 wt-% of an ethylene-vinyl acetate copolymer comprising about 40-60 wt-% vinyl acetate; and

(d) about 30-50 wt-% of an alphamethyl styrene tackifier resin.

25

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/02216

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>1</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C08G18/10 ; C08G18/42 ; C08G18/76 ; C09J3/00

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>2</sup>

Classification System	Classification Symbols
Int.C1. 5	C08G ; C09J

Documentation Searched other than Minimum Documentation  
in the Extent that such Documents are included in the Fields Searched<sup>3</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>4</sup>

Category <sup>5</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	DE,A,2014170 (TEIJIN) 15 October 1970 see page 4, line 18 - page 7, line 23; claim 1; example 1 ---	1-11, 14-24, 30-40
A	EP,A,0248658 (SCOTT BADER) 09 December 1987 see page 2, line 24 - page 5, line 12; claims 1-13 ---	1
A	EP,A,0125009 (BOSTIK) 14 November 1984 see page 6, line 22 - page 8, line 20; claims 1, 3, 6 ---	1
A	US,A,4206299 (YAMAZAKI ET AL) 03 June 1980 see column 2, line 53 - column 4, line 29; claims 1-5 ---	1, 12, 13 -/-

\* Special categories of cited documents :<sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"R" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

1 24 JUNE 1991

Date of Mailing of this International Search Report

12.07.91

International Searching Authority

EURPEAN PATENT OFFICE

Signature of Authorized Officer

BOURGONJE A. F.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>Adhesive Age            November 1987, Atlanta, GA, US            pages 32 - 35; Huber et al.:            "Shaping Reactive Hot Melts Using LMW            Copolyesters"            see the whole document</p> <p>---</p>	1
A	<p>EP,A,0289945 (H.B. FULLER) 09 November 1988            see the whole document            &amp; US,A,4808255            (cited in the application)</p> <p>---</p>	1-50
A	<p>EP,A,0293602 (H.B. FULLER) 07 December 1988            see the whole document            &amp; US,A,4820368            (cited in the application)</p> <p>----</p>	1-50

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9102216  
SA 46571

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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EP-A-0248658	09-12-87	None		
EP-A-0125009	14-11-84	GB-A- AU-B- AU-A- AU-B- AU-A- CA-A- EP-A, B JP-A- JP-A- US-A-	2137638 568540 2639984 569504 2640084 1225492 0125008 59197201 59197482 4618651	10-10-84 07-01-88 11-10-84 04-02-88 11-10-84 11-08-87 14-11-84 08-11-84 09-11-84 21-10-86
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EP-A-0289945	09-11-88	US-A- JP-A-	4808255 1054087	28-02-89 01-03-89
EP-A-0293602	07-12-88	US-A- JP-A-	4820368 1054089	11-04-89 01-03-89

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82